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<p>(54) Title: THERMOPLASTIC POLYBUTYLENE TEREPHTHALATE COMPOSITIONS FOR WIRE COATING APPLI- CATIONS</p> <p>(57) Abstract</p> <p>Thermoplastic compositions based on polybutylene terephthalate are provided which are useful in high temperature resis- tant wire coating applications. These compositions generally are four-component alloys containing a) 40-65 % by weight of poly (1,4-butylene terephthalate); b) 1-30 % by weight of a polymeric grafting agent which is an ethylene copolymer carrying reactive groups; c) 0-20 % by weight of an ethylene copolymer ionomer; d) at least one component selected from the group of a copolyes- ter urethane, a copolyether ester, a hydrogenated styrene/diene block copolymer optionally grafted with maleic anhydride, an ad- duct of maleic anhydride and a copolymer of ethylene or an acrylic-modified elastomer-based polymer.</p>		

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TITLE

THERMOPLASTIC POLYBUTYLENE TEREPHTHALATE COMPOSITIONS
FOR WIRE COATING APPLICATIONS

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CROSS-REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of United States Application Serial No. 07/781,459; filed October 24, 1991.

Background of the Invention10 Field of Invention:

This invention relates to thermoplastic compositions useful in wire coating applications and more particularly to such compositions which are halogen-free and useful in high temperature resistant wire coating applications.

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Background Problems and Art:

Due to the increasing density of components under the hood of today's high performance cars, temperature requirements of the insulation materials of wires and cables used in such applications become more and more demanding. This is the more important as the current working horse for these applications, polyvinyl chloride (PVC) is being considered more and more as an environmental threat, and the industry is therefore looking for a halogen-free, thermoplastic and high temperature resistant material which would fulfil the requirements of today's cars and be able to replace PVC at the same time. Today's requirements consist of retaining sufficient elongation after 3000h at 135° C while showing a minimum of discoloration, good chemical resistance, and good low temperature flexibility.

Some materials described in published European Patent Application No. EP-290 588-A (Saltman) have been found to meet these requirements. This patent application describes elastomeric thermoplastic polymers prepared by meltgrafting three components: an engineering thermoplastic (e.g. nylon, polyester, copolyester ether, copolyester ester, or polycarbonate), an ionomer, and a polymeric grafting agent. In particular, this patent application describes polymer alloys which comprise, in general:

35

a) 25-50% volume of at least one thermoplastic resin;

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- 5 b) 10-74% volume of at least one ethylene copolymer E/X/Y where
E is > 50%wt ethylene X is 1-35%wt of an acid-
containing unsaturated monocarboxylic acid and
Y is 0-49%wt of a moiety derived from at least
one alkyl acrylate, alkylmethacrylate, vinyl ether,
carbon monoxide, sulfur dioxide, or mixtures
thereof, where the alkyl and ether radicals
contain 1-12 carbon atoms and further wherein
the acid groups in the acid-containing moiety are
neutralized from 0-100% by a metal ion;
- 10 c) 1-50% volume of at least one polymeric grafting agent which
contains reactive groups selected from at least
one of epoxides, isocyanates, aziridine silanes,
alkylating agents, that react with the acid-
containing moieties in component b) and that
15 additionally react with the reactive graft sites of
component a).

The aforesaid EP-290 588-A describes various elastomeric
thermoplastic polymer compositions having good high temperature
20 properties. For wire and cable (W and C) coatings, such coatings must show
a minimal degradation of properties after ageing 3000 hours at 135° C. Other
thermoplastic resins which do not contain any reactive groups are described
in U.S. Patent 4,871,810 (Saltman).

Alloys within EP-290 588 where the engineering thermoplastic is
25 based on nylon 6 or nylon 6.6 and which contain around 50% of engineering
thermoplastic resin, 5% of component c) and 45% of component b) show
excellent ageing characteristics, good abrasion resistance, excellent low
temperature flexibility and good hydrolytic resistance. Also the chemical
resistance is outstanding. With these properties, these materials can be used
30 for under the hood applications where a continuous service temperature of
135° - 140° C is required.

At higher temperatures, i.e., about 150° C, materials based on nylon
are less useful for under the hood applications since they show marked
degradation of properties. Therefore, an engineering polymer within EP-290
35 588-A having a higher temperature resistance should be used, such as a
polyester-based alloy. Polybutylene terephthalate (PBT) is selected as the

base engineering thermoplastic because it is known to have a higher temperature resistance, better wet electrical properties and to show less discoloration after ageing; a lower abrasion resistance is a known disadvantage. It was discovered, however, that the ageing performance of
5 PBT-based alloys in extruded wire coatings is inferior to the compositionally identical plaque stock.

SUMMARY OF THE INVENTION

According to the present invention there is provided a partially
10 grafted, flexible thermoplastic composition formed by melt blending comprising:

- (a) 40 - 65% by weight of poly (1,4-butylene) terephthalate;
- (b) 1 - 30% by weight of a polymeric grafting agent which is a
15 copolymer of at least 50% by weight ethylene, 0.5 - 15% by weight of at least one reactive moiety selected from the group consisting of (i) an unsaturated epoxide of 4 - 11 carbon atoms, (ii) an unsaturated isocyanate of 2 - 11 carbon atoms, (iii) an alkoxy or alkyl silane wherein the alkyl group is from 1 - 12
20 carbon atoms, (iv) an alkyl halide, (v) an alkyl alpha-halo ketone or aldehyde, and (vi) oxazoline, and 0-49% by weight of a moiety selected from at least one of an alkyl acrylate, alkyl methacrylate, vinyl ether, carbon monoxide, and sulfur dioxide, where the alkyl and ether groups above are of 1 - 12 carbon atoms;
- 25 (c) 0 - 20% by weight of an ethylene copolymer which comprises at least 50% by weight of ethylene, 1 - 35% by weight of an acid-containing unsaturated mono-carboxylic acid, and 0-49% by weight of a moiety selected from at least one of alkyl acrylate, alkyl methacrylate, vinyl ether, carbon monoxide and sulfur
30 dioxide, and further wherein the acid groups are neutralized from 0-100% by a metal ion; and
- (d) at least one of:
 - 35 (i) 0 - 25% by weight of a thermoplastic elastomer selected from the group consisting of a copolyester ester and a copolyether ester;

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- 5 (ii) 0 - 45% by weight of a styrene/diene block copolymer, with 3 or more sequences, of the $S-(D-S)_n$ structure where n is a whole number, S is a polystyrene block, D is a hydrogenated isoprenic block or hydrogenated butadienic block, with a content in styrene less than 50% by weight optionally grafted with maleic anhydride;
- (iii) 0-25% by weight of an adduct of maleic anhydride and a copolymer of ethylene, at least one C_3 to C_6 alphaolefin, and at least one nonconjugated diene; or
- 10 (iv) 0 - 25% by weight of an acrylic-modified elastomer-based polymer wherein the elastomeric portion is polymerized from a monomer mixture containing at least 50% by weight of at least one C_1 to C_{15} alkyl acrylate, 0 - 5% by weight of at least one graftlinking monomer, 0 - 5% by weight of a crosslinking
- 15 monomer, and the balance to 100% by weight of at least other polymerizable ethylenically unsaturated monomer;
- provided that:
- (1) the total of (a) - (d) is 100%;
- (2) the total polyester content of (a) and (d) (i) does not exceed 70%;
- 20 and
- (3) if (c) is 0%, then (d) cannot be (i), (iii), and (iv), and (ii) can be 10 - 45% by weight.

Also provided is an insulated wire which comprises an electrically conductive wire having a coating thereon of one of the aforesaid

25 compositions.

DETAILED DESCRIPTION OF THE INVENTION

The compositions of the present invention are partially grafted, flexible thermoplastic 3- or 4-component alloys based on poly (1,4-butylene) terephthalate (PBT). These PBT alloys, when extruded as wire coatings,

30 show minimal discoloration and a retention of mechanical properties after ageing 3000 hours at 150°C (e.g., at least 50% of elongation at break is retained).

The phrase "partially grafted" is meant to indicate that in the

35 compositions of the present invention the grafting agent is the limiting component, i.e., the addition of more grafting agent than is permitted by the

definition of this invention would result in further grafting and the creation of an intractable composition.

In particular, this invention relates to partially grafted flexible thermoplastic compositions based on PBT.

5 The three or four components described above are melt blended with each other under high shear. The various ingredients may first be combined with one another in what is commonly referred to as a "salt and pepper" blend, i.e., a pellet blend, of each of the ingredients, or they may be combined with one another via simultaneous or separate metering of the
10 various components, or they may be divided and blended in one or more passes into one or more sections of mixing equipment such as an extruder, Banbury, Buss Kneader, Farrell continuous mixer, or other mixing equipment. For example, one can use an extruder with two or more feed zones into which one or more of the ingredients may be added sequentially.
15 In this case, it is sometimes advantageous that the thermoplastic and polymeric grafting component be combined first, then the acid-containing copolymer be added downstream. This helps promote the grafting reaction(s) between the thermoplastic and polymeric grafting components, prior to the reaction(s) between the polymeric grafting component and acid-
20 containing copolymer. However, the order of addition does not have any effect on the high temperature properties described by this invention. The high shear insures proper dispersion of all the components such as would be necessary to carry out the grafting reaction. In addition, sufficient mixing is essential to achieve the morphology which is necessary in the compositions of
25 the present invention. The morphology required for the compositions of the present invention is that at least one of continuous phases must be the thermoplastic; i.e., component (a).

 The PBT base thermoplastic resin (a) useful in this invention has a number average molecular weight greater than 7500, preferably greater than
30 10,000. Such resins are available commercially. The compositions of the invention contain generally 40-65% by weight PBT with the preferred content depending upon the composition and content of the other three components. Preferably, the compositions contain between 50 and 65% by weight PBT; the total polyester content of the compositions being no greater
35 than 65% otherwise the compositions will be too stiff and have inferior ageing properties.

Polymeric grafting agents (b) useful in the compositions of the inventions are ethylene copolymers copolymerized with one or more reactive moieties selected from unsaturated epoxides of 4 - 11 carbon atoms, such as glycidyl acrylate, glycidyl methacrylate, allyl glycidyl ether, vinyl glycidyl ether, and glycidyl itaconate, unsaturated isocyanates of 2 - 11 carbon atoms, such as vinyl isocyanate and isocyanato-ethyl methacrylate, aziridine, silanes such as alkoxy or alkyl silanes, alkylating agents such as alkyl halides or alpha-halo ketones or aldehydes or oxazoline and may additionally contain an alkyl acrylate, alkyl methacrylate, carbon monoxide, sulfur dioxide and/or vinyl ether, where the alkyl radical is from 1 - 12 carbon atoms.

In particular, the polymeric grafting agent is a copolymer of at least 50% by weight ethylene, 0.5 - 15% by weight of at least one reactive moiety selected from the group consisting of (i) an unsaturated epoxide of 4 - 11 carbon atoms, (ii) an unsaturated isocyanate of 2 - 11 carbon atoms, (iii) an alkoxy or alkyl silane wherein the alkyl group is from 1 - 12 carbon atoms, (iv) an alkyl halide, (v) an alkyl alpha-halo ketone or aldehyde, and (vi) oxazoline, and 0-49% by weight of a moiety selected from at least one of an alkyl acrylate, alkyl methacrylate, vinyl ether, carbon monoxide, and sulfur dioxide, where the alkyl and ether groups above are of 1 - 12 carbon atoms.

Preferred polymeric grafting agents for use in the compositions of the present invention include ethylene/glycidyl acrylate, ethylene/n-butyl acrylate/glycidyl acrylate, ethylene/methylacrylate/glycidyl acrylate, ethylene/glycidyl methacrylate, ethylene/n-butyl acrylate/glycidyl methacrylate and ethylene/methylacrylate/glycidyl methacrylate copolymers. The most preferred grafting agents for use in the compositions of the present invention are copolymers derived from ethylene/n-butyl acrylate/glycidyl methacrylate and ethylene/glycidyl methacrylate.

A preferred polymeric grafting agent is a copolymer of at least 55% by weight ethylene, 1-10% by weight of an unsaturated epoxide of 4-11 carbon atoms, and 0-35% by weight of at least one alkyl acrylate, alkyl methacrylate, or mixtures thereof where the alkyl groups contain 1-8 carbon atoms. Preferred unsaturated epoxides are glycidyl methacrylate and glycidyl acrylate which are present in the copolymer at a level of 1-7% by weight. Preferably, ethylene content is greater than 60% by weight and the third moiety is selected from methyl acrylate, iso-butyl acrylate, and n-butyl acrylate.

The polymeric grafting agents concentration in the compositions of the invention is 1-30% by weight, preferably 2 or 5 to 15 or 20% or even to 30% by weight depending upon the nature and content of the other components.

5 Ethylene copolymers (c) useful in the present invention comprise at least 50% by weight of ethylene, 1 - 35% by weight of an acid-containing unsaturated mono-carboxylic acid, and 0-49% by weight of a moiety selected from at least one of alkyl acrylate, alkyl methacrylate, vinyl ether, carbon
10 monoxide and sulfur dioxide, and further wherein the acid groups are neutralized from 0-100% by a metal ion;

 Preferred ethylene copolymers comprise at least 60% by weight of ethylene, 5 - 15% by weight of acrylic acid or methacrylic acid, and 0 - 25% by weight of a moiety selected from at least one of methyl acrylate, iso-butyl
15 acrylate and n-butyl acrylate, and further wherein the acid groups are neutralized from 0 - 70%, preferably from 30 - 70%, by at least one metal ion selected from lithium, potassium, sodium, zinc, magnesium, aluminium, and calcium.

 Suitable preferred ethylene copolymers include ethylene/acrylic acid, ethylene/methacrylic acid, ethylene/acrylic acid/n-butyl acrylate,
20 ethylene/methacrylic acid/n-butyl acrylate, ethylene/methacrylic acid/iso-butyl acrylate, ethylene/acrylic acid/iso-butyl acrylate, ethylene/methacrylate acid/n-butyl methacrylate, ethylene/acrylic acid/methyl methacrylate, ethylene/acrylic acid/ethyl vinyl ether,
 ethylene/methacrylic acid/butyl vinyl ether ethylene/acrylic acid/methyl
25 acrylate, ethylene/methacrylic acid/methyl acrylate, ethylene/methacrylic acid/methyl methacrylate, ethylene/acrylic acid/n-butyl methacrylate, ethylene/methacrylic acid/ethyl vinyl ether and ethylene/acrylic acid/butyl vinyl ether. The most preferred ethylene copolymers for use in the
 compositions of the present invention are ethylene/methacrylic acid,
30 ethylene/acrylic acid copolymers, ethylene/methacrylic acid/n-butyl acrylate and ethylene/methacrylic acid/methylacrylate terpolymers.

 The ethylene copolymer concentration in the compositions of the invention is 0-20% by weight, provided that when there is 0 ethylene
 copolymer present, then a 3-component composition is possible with
35 styrene/diene block copolymer (d) (ii). Also, when more than 15% by weight ethylene copolymer is present, then a thermoplastic elastomer (d) (i)

and/or a styrene/diene block copolymer (d) (ii) should be present in the composition. The preferred ethylene copolymer concentration in the compositions of the invention depend on the nature and content of the other components, but will generally be from 5 - 15% by weight.

5 Thermoplastic elastomers (d) (i) useful in the compositions of this invention are copolyester esters and copolyether esters. Copolyether esters are preferred and are described in U.S. Patent 4,221,703 to Hoeschele, the disclosure of which is herein incorporated by reference. Preferred
10 copolyether esters are prepared from dimethyl terephthalate, 1,4-butanediol, and poly (tetramethylene oxide) glycol having a molecular weight of about 600 - 2000 or poly(ethylene oxide) glycol having a molecular weight of about 600 - 1500. Optionally, up to about 30 mole % and preferably 5 - 20 mole % of the dimethyl terephthalate in these polymers can be replaced by dimethyl
15 phthalate or dimethyl isophthalate. Other preferred copolyesters are those prepared from dimethyl terephthalate, 1,4-butanediol, and poly(propylene oxide) glycol having a molecular weight of about 600 - 1600. Up to 30 mole % and preferable 10 - 25 mole % of the dimethyl terephthalate can be replaced with dimethyl isophthalate or butanediol can be replaced with
20 neopentyl glycol until up to about 30% and preferably 10 - 25% of the short chain ester units are derived from neopentyl glycol in these poly(propylene oxide) glycol polymers.

Copolyester ester elastomers are described in EP-013461 to Huntjens, the disclosure of which is herein incorporated by reference. Preferred
25 copolyester esters are prepared from polybutylene adipate of various molecular weights and aliphatic or aromatic diisocyanates, particularly toluene diisocyanate, having a molecular weight in the range of 500 - 5000.

The concentration of thermoplastic elastomers in the compositions is 0-25% by weight. In general, these elastomers are used when ethylene
30 copolymer (c) is used at a concentration greater than 15% by weight. The elastomers are used to complement the thermoplastic PBT phase so as to obtain higher abrasion resistance, higher flexibility, lower discoloration, improved ageing performance after extrusion, and improved chemical resistance. When used in wire coating applications, the total polyester content should not exceed 70%. A particularly beneficial composition for
35 wire coating applications comprises:

- (a) 40 - 65% by weight PBT;
- (b) 2 - 30% by weight of a preferred polymeric grafting agent;
- (c) 0 - 20% by weight of a preferred ethylene copolymer; and
- (d) 10 - 25% by weight of a preferred copolyether ester;

5 Another particularly beneficial composition comprises:

- (a) 40 - 65% by weight PBT;
- (b) 5 - 20% by weight of a preferred polymeric grafting agent;
- (c) 10 - 20% by weight of a preferred ethylene copolymer; and
- (d) 10 - 20% by weight of a preferred copolyether ester.

10 Still another comprises:

- (a) 40 - 65% by weight PBT;
- (b) 2 - 30% by weight of a preferred polymeric grafting agent;
- (c) 0 - 20% by weight of a preferred ethylene copolymer;
- (d) (i) 5 - 15% by weight of a preferred copolyether ester; and
- 15 (iv) 5 - 15% by weight of a preferred acrylic modified, elastomer based on polymer as described below.

and still another comprises:

- (a) 40 - 65% by weight PBT;
- (b) 2 - 30% by weight of a preferred polymeric grafting agent;
- 20 (c) 0 - 20% by weight of a preferred ethylene copolymer; and
- (d) (i) 5 - 15% by weight of a preferred copolyether ester
- (iii) 5 - 15% by weight of a preferred "maleic anhydride adduct of an ethylene copolymer as described below".

25 The concentration of styrene/diene block copolymers (d) (ii) in the composition is 0-45% by weight. In general, these copolymers replace all or part of ethylene copolymer (c) in the composition. Useful styrene/diene block copolymers are described in U.S. Patent 4,548,988 to Castelein, the disclosure of which is incorporated by reference. In general, these copolymers have 3 or more sequences of the S-(D-S)_n structure where n is a

30 whole number, S is a polystyrene block, D is a hydrogenated isoprenic block or hydrogenated butadienic block, with a content in styrene less than 50% by weight. Optionally, these block copolymers can be grafted with maleic anhydride so as to form adducts which contain 0.1 to 10% by weight, preferably 0.2 to 5%, of maleic anhydride (see U.S. Patent 4,578,429).

35 A particularly beneficial composition for wire coating applications comprises:

- (a) 50 - 65% by weight of PBT;
- (b) 5 - 15% by weight of a preferred polymeric grafting agent;
- (c) 0 - 10% by weight of a preferred ethylene copolymer; and
- (d) 20 - 45% by weight of a preferred styrene/diene block copolymer.

5 The concentration of an adduct of maleic anhydride and an ethylene copolymer (d) (iii) in the composition is 0-25% by weight. Useful adducts of maleic anhydride with an ethylene copolymer and their preparation are described in U.S. Patent 3,884,887 and U.S. Re. 31,680, both to Caywood, the disclosures of which are incorporated by reference. These elastomeric
10 copolymers of ethylene are composed of ethylene, at least one C₃ to C₆ alpha-olefin, preferably propylene, and at least one nonconjugated diene, preferably 1,4 hexadiene alone or with 2,5-norbornadiene. The maleic anhydride content of the adduct is 0.5 to 9% by weight, preferably 1-4% by weight; and the adduct has an inherent viscosity of at least 1, preferably at
15 least 1.5, as measured on 0.1 gram of adduct copolymer dissolved in 100 milliliters of perchloroethylene at 30° C. A particularly beneficial composition for wire coating applications comprises:

- (a) 50 - 65% by weight PBT;
- (b) 5 - 15% by weight of a preferred polymeric grafting agent;
- 20 (c) 5 - 10% by weight of a preferred ethylene copolymer; and
- (d) 10 - 25% by weight of a preferred maleic anhydride adduct of an ethylene copolymer.

 The concentration of acrylic-modified elastomer-based polymer (d) (iv) in the composition is 0-25% by weight. In general, these polymers are
25 also used with low concentrations of ethylene copolymer (c). Useful acrylic-modified elastomeric-based polymers and their preparation are described in U.S. Patent 4,167,505 to Dunkelberger, the disclosure of which is incorporated by reference. Those described in column 4, lines 39-55 are most preferred.

30 The acrylic-elastomer polymers have an elastomeric portion which is polymerized from a monomer mixture containing at least 50% by weight of at least one C₁ to C₁₅ alkyl acrylate, 0 - 5% by weight of at least one graftlinking monomer, 0 - 5% by weight of a crosslinking monomer, and the balance to 100% by weight of at least other polymerizable ethylenically
35 unsaturated monomer. Suitable graftlinking monomers and crosslinking monomers are described in column 3, lines 34 - 48 of U.S. Patent 4,167,505.

Preferred polymers are an elastomeric-based acrylic core//shell polymer having:

- 5 (1) 70 - 80 parts by weight of a first acrylic elastomeric stage comprising a polymer polymerized from a monomer mixture comprising 79 - 99.5 parts n-butyl acrylate, 0 - 10 parts of at least one polymerizable monoethylenically or conjugated diethylenically unsaturated monomer, 0.1 - 5 parts 1,4-butylene glycol diacrylate and 0.1 - 5 parts diallyl maleate; and
- 10 (2) 20 - 30 parts by weight hard shell final stage polymer polymerized in the presence of said first elastomeric stage from a monomer mixture comprising about 80 - 100 parts by weight methyl methacrylate, 0 - 20 parts of another monoethylenically unsaturated monomer and 0 - 5 parts monoethylenically

A particularly beneficial composition for wire coating applications comprises:

- 15 (a) 50 - 65% by weight PBT;
- (b) 5 - 20% by weight of a preferred polymeric grafting agent;
- (c) 5 - 15% by weight of a preferred ethylene copolymer; and
- 20 (d) 15-25% by weight of a most preferred acrylic-modified elastomer-based polymer.

The composition of the present invention totals 100% of components (a) - (d). Of course, the compositions can include other ingredients as are customarily used in the conventional compounding of thermoplastics, provided that such other ingredients are no more than 100 parts by weight
25 per 100 parts by weight of components (a) - (d). Examples of such other ingredients include carbon black, metal deactivators, glass fibers, graphite fibers, KEVLAR® (aramid) fibers, glass spheres, plasticizers, lubricants, silica, titanium dioxide, pigments, clay, mica and other mineral fillers, flame retardants, antioxidants, ultraviolet stabilizers, heat stabilizers, processing
30 aids, adhesives and tackifiers.

The invention can be further understood by the following examples in which parts and percentages are by weight unless indicated otherwise and temperatures are in degrees Celsius.

The invention is a thermoplastic elastomer composition based on PBT
35 containing a grafting component which is prepared by melt blending and is preferably used for applications in wire and cable insulations intended for

automotive under the hood applications. These compositions show high temperature resistance, good low temperature flexibility, superior chemical resistance as well as high abrasion resistance.

- The process for preparing the compositions and the insulation of the wire includes:
1. Careful drying of all the major ingredients.
 2. Preparing a pellet blend together with the antioxidants in a tumble blender.
 3. Melt blending and melt grafting of the blend in a twin screw extruder.
 4. Pelletizing the strands by a strand cutter.
 5. Drying of the pellets.
 6. Extruding the blends onto wire.
 7. Injection molding of test plaques. Instead of applications in wire coating the aforementioned blends have also shown utility in injection molding, and due to the increased viscosity, in blow molding applications.

Description of Process Steps

1. The preparation of the pellet blend was undertaken in the following manner:
Polyester is usually dried for 3 hours at 110° C under vacuum, thermoplastic copolyesters, 3 hours at 100° C, elastomeric ingredients several hours at 80° C and the ionomer for at least 24 hours at 40° C under dry nitrogen purge. The moisture content of none of the ingredients should be higher than 0.05%.
 2. After drying, the components were weighed and pellet blended, antioxidants were added. Then they were mixed in a tumble blender.
 3. For meltblending, a 24 mm Berstorff twin screw extruder was used. A high shear screw design was used to melt blend these compositions in order to obtain intimate mixing of the components and favorable properties.
- The temperature profile which was applied for compositions of this invention was the following:

Zone	1	2	3	4	5	6	Die	Melt
Temp. (°C)	200	235	235	235	235	240	240	255- 270

- Usually a screw speed of 180 - 200 rpm was used which leads to a compounding speed of approximately 7-14 kg/h. Meltgrafted compositions can also be prepared using twin screw extruders of different sizes, using internal mixers (Brabenders), using Banburies and

Farrell continuous mixers, and by feeding of the components of the compositions through different ports of the mixing devices.

4. The extruded strands were cooled in a waterbath and cut with a strandcutter into pellets.

5. The pelletized resin was dried for at least 3 hours at 110° C to a moisture level of less than 0.05% and then placed in heat sealed bags.

6. Extrusion onto wire:

In order to extrude the compositions onto wire, a 30 mm Maillefer wire coating line was used. Usually, a barrier screw (design "ELISE") was used for extrusion, but metering screws with a compression ratio ranging from 2:1 to 4:1 as well as metering screws with Maddox Mixing heads are preferred. The output of the extruder at maximum screw speed was around 7.5 kg/h.

For the coating process a B + H 75 Crosshead was used with a pressure extrusion set-up attached to it. But also tubing extrusion is possible and was found to lead to good results. For pressure extrusion, the die was chosen with a diameter usually 20% bigger than the wire diameter.

The following temperature profile was applied:

20

	1	2	3	4	Adapt	Xhead	Die	Melt	Stock
T(°C)	210	235	240	240	250	250	250	249	275

The materials were extruded on stranded bare copper wires. Two constructions were used: AWG 20, 7s (OD 0.97mm) and 19 X .23 (0.75mm*2) (OD 1.12mm).

25 The compositions were then stripped off the copper wire using an insulation stripping device. The tubes (0.25 - 0.35 mm wall thickness) obtained by this method were aged in air circulated ovens for 24 hours at room temperature (50% R.H.).

30 A number of physical properties were measured for each composition. Unless otherwise noted, the samples were prepared and tested as follows. Melt Indices of the ethylene copolymers and the grafting agents were determined according to ASTM D-1238. Tensile properties (elastic modulus, tensile strength and elongation) at room temperature, 150° C, 165° C, and 35 180° C were measured by Procedure IEC 540-5.1.. Percent retention of tensile strength at break was calculated from the individual reading taken at the elevated temperature as compared with room temperature readings. All of the samples were conditioned for at least 24 hours at 50% RH.

40 Other tests performed include wrapttest (DIN 72551 - part 5 item 3.4.8), and the scrape abrasion test (DIN 72551 - part 5 item 3.3.3.). The

thermoplastics, grafting agents, ethylene copolymers, and additives used in the Examples are set forth below.

In the following Examples, all percentages of components a-d are given by weight. All additives are given in parts per hundred based on the weight of components a-d.

The components and additives used in the examples are as follows:

- a = polybutylene terephthalate having a density (g/cc) of 1.34 and a melt index (2160 g weight) of 8 @ 240° C.
- b = a copolymer of 64.9% by weight ethylene, 28% by weight n-butyl acrylate, and 5.25% by weight of glycidyl methacrylate having a density (g/cc) of 0.94 and a melt index at 190 °C/2.16 kg (g/10min) of 20.0.
- c = a copolymer of 66.9% by weight ethylene, 24.5% by weight of n-butyl acrylate, and 8.6% by weight of methacrylic acid neutralized at about 50% with Na ion. This polymer has a density (g/cc) of 0.94 and a melt index at 190 °C/2.16 kg (g/10min) of 1.0.
- d (1) = a copolyester ester elastomer sold by Akzo N.V. as Arnitel® UM 550.
- (2) = a copolyether ester elastomer with 75% by weight butyleneterephthalate units and 25% by weight polytetramethylene ether (1000 Mn) terephthalate having a melt index (2160g) of 13 at 220° C.
- (3) = a styrene/diene block copolymer sold by Shell Chemicals as Kraton® FG 1902X.
- (4) = a maleic anhydride adduct of an ethylene copolymer which is about 68% by weight ethylene, 26% by weight propylene, 6.3% by weight of 1,4-hexadiene, and 0.13% by weight of 2,5-norbornadiene grafted with fumaric acid to contain 1.5-2% maleic anhydride (melt index of 1-5g/10 min.).
- (5) = an acrylic-modified polycarbonamide elastomer sold by Rohm and Haas Company as Paraloid® EXL 3373.

The additives used are the same for all examples; a blend of commercially available primary and secondary anti-oxidants and a metal deactivator.

TABLE I

Polybutylene Terephthalate Thermoplastic
Elastomer Compositions

10

Ex. No.	wt % a	wt % b	wt % c	wt % d (No.)	wt % Additives
Control 1	50.0	2.5	47.5	-	2.3
Control 2	50.0	5.0	45.0	-	2.3
Control 3	62.5	4.5	33.0	-	2.3
Control 4	50.0	5.0	45.0	-	3.8
1	50.0	20.0	15.0	15(2)	3.8
2	50.0	25.0	10.0	15(2)	3.8
3	50.0	30.0	5.0	15(2)	3.8
4	40.0	20.0	15.0	25(2)	3.8
5	50.0	20.0	10.0	20(2)	3.8
6	50.0	20.0	15.0	15(1)	3.8
7	50.0	25.0	10.0	15(1)	3.8
Control 5	65.0	5.0	-	30(4)	3.8
8	65.0	5.0	10.0	20(4)	3.8
9	50.0	5.0	-	45(3)	3.8
10	65.0	5.0	-	30(3)	3.8
11	50.0	10.0	15.0	25(5)	3.8
12	50.0	20.0	5.0	25(5)	3.8
13	60.0	20.0	5.0	15(5)	3.8
Control 6	50.0	5.0	45.0	---	3.8
14	50.0	25.0	10.0*	15(2)	3.8
15	50.0	20.0	15.0	7.5(2)	3.8
16	60.0	10.0	10.0	7.5(2)	3.8
17	50.0	25.0	10.0	15(2)	17.8**
18	50.0	27.0	8.0	15(2)	17.8**
19	50.0	25.0	0	25(2)	3.8

* 0% neutralization; MI of 30.

** Fire retardant includes 10% tetradecabromodisphenoxylbenzene and 4% Sb₂O₃

Physical properties were measured on test plaques and coated wire made from these compositions. The results are shown in Table II.

TABLE II

Physical Properties of Compositions of Table I

Ex. No.	Plaque (as made)		Wire Tube (as made)		Plaque (Aged)		Tube Wire (Stripped & Aged)	
	TS Break 230MPa	% Elong Br. 23C	TS Br. 230MPa	% Elong. Br. 23C	TS 165C/2wk	% Elong. 165C/2wk	TS 165C/2w	% Elong. 165C/2w
Ctrl. 1	---	---	1.7	349	---	---	20.5	20.
Ctrl. 2	25.8	318	3.0	305	279	21.4	21.3	82
Ctrl. 3	26.9	255	6.0	316	239	29.0	26.1	151
Ctrl. 4	25.2	257	8.4	259	27.2	25.7	21.1	165
1	29.5	230	2.4	244	32.8	32.8	27.1	124
2	32.5	276	2.3	187	32.6	---	27.7	26.
3	---	---	9.5	130	---	---	124	28.
4	---	---	22	234	---	---	24.2	25.
5	---	---	4.4	208	---	---	25.3	25.
6	20.9	200	2.4	231	160	---	28.6	108
7	---	---	0.0	214	---	---	27.6	126
Ctrl. 5	---	---	0.0	158	---	---	24.7	145
8	27.9	240	2.6	225	28.4	---	23.0	96
9	---	---	0.8	308	---	---	28.6	122
10	---	---	0.0	230	---	---	24.0	220
11	---	---	9.1	166	---	---	28.7	119
12	18.7	191	6.2	120	---	---	22.5	111
13	---	---	1.3	107	27.1	---	21.1	20.
Ctrl. 6	---	---	3.5	75	---	---	26.0	84
14	---	---	3.6	325	---	---	22.5	173
15	---	---	4.9	284	---	---	33	168
16	---	---	2.7	203	---	---	28.1	155
17	---	---	6.6	259	---	---	27.3	148
18	---	---	22	174	---	---	27.9	135
19	---	---	5.4	423	---	---	26.3	84
					---	---	33.5	224
					---	---	---	31.
					---	---	---	205

TABLE II (continued)
Physical Properties of Compositions of Table I

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Ex. No.	Tube Color after 180° C/1 wk (%)	Tube Abra. Resistance (%)	Tube retention of TS + % Elong. after ageing 3000 hr/150° on wire			Processing Wire Coating
			Wrap Test	Ret. TS	Ret. Elong	
Control 1	dk. brown	443	pass	---	0	good
Control 2	black	492	fail	102	2	good
Control 3	dk. brown	485	pass	108	5	good
Control 4	dk. brown	577	pass	93	19	good
1	tan	1507	pass	124	53	good
2	lt. tan	1735	pass	124	53	good
3	lt. tan	1149	pass	---	---	good
4	lt. tan	1825	pass	115	30	good
5	lt. tan	1990	pass	119	40	good
6	lt. brown	1171	pass	108	34	good
7	lt. brown	952	pass	125	71	good
Control 5	yellow	842	pass	82	9	poor
8	yellow	1141	pass	121	58	good
9	yellow	212	pass	87	43	good
10	yellow	336	pass	124	25	good
11	br. yellow	1195	pass	116	58	good
12	br. yellow	868	pass	136	99	good
13	yellow	986	pass	134	131	good
Control 6	lt. yellow	117	---	---	---	
14	dk. brown	953	---	---	---	
15	brown	969	pass	90.7	50	
16	lt. yellow	1005	pass	99.6	36	
17	lt. tan	1529	pass	94.6	42	
18	lt. tan	n/a	11/3/92*	---	---	
19	tan	1118	pass	---	---	

10 *Test results expected 11/92

15 The results of the above examples show that the compositions of the invention have a better retention of elongation after ageing on wire than the control compositions. The compositions of the invention also have better color retention than the control compositions. It is surprising when component (c) is reduced and partially replaced with component (d) and/or (b), that ageing properties of the coatings on wire are improved versus the measurement of the same properties on plaques (particularly elongation and discoloration).

20

WHAT IS CLAIMED IS:

1. A partially grafted, flexible thermoplastic composition formed by melt blending comprising:
- 5
- (a) 40 - 65% by weight of poly (1,4-butylene) terephthalate;
- (b) 1 - 30% by weight of a polymeric grafting agent which is a copolymer of at least 50% by weight ethylene, 0.5 - 15% by weight of at least one reactive moiety selected from the group consisting of (i) an unsaturated epoxide of 4 - 11 carbon atoms, (ii) an unsaturated isocyanate of 2 - 11 carbon atoms, (iii) an alkoxy or alkyl silane wherein the alkyl group is from 1 - 12 carbon atoms, (iv) an alkyl halide, (v) an alkyl alpha-halo ketone or aldehyde, and (vi) oxazoline, and 0-49% by weight of a moiety selected from at least one of an alkyl acrylate, alkyl methacrylate, vinyl ether, carbon monoxide, and sulfur dioxide, where the alkyl and ether groups above are of 1 - 12 carbon atoms;
- 10
- (c) 0 - 20% by weight of an ethylene copolymer which comprises at least 50% by weight of ethylene, 1 - 35% by weight of an acid-containing unsaturated mono-carboxylic acid, and 0-49% by weight of a moiety selected from at least one of alkyl acrylate, alkyl methacrylate, vinyl ether, carbon monoxide and sulfur dioxide, and further wherein the acid groups are neutralized from 0-100% by a metal ion; and
- 15
- 20
- 25
- (d) at least one of:
- (i) 0 - 25% by weight of a thermoplastic elastomer selected from the group consisting of a copolyester ester and a copolyether ester;
- 30
- (ii) 0 - 45% by weight of a styrene/diene block copolymer, with 3 or more sequences, of the S-(D-S)_n structure where n is a whole number, S is a polystyrene block, D is a hydrogenated isoprenic block or hydrogenated butadienic block, with a content in styrene less than 50% by weight optionally grafted with maleic anhydride;
- 35

- (iii) 0-25% by weight of an adduct of maleic anhydride and a copolymer of ethylene, at least one C₃ to C₆ alphaolefin, and at least one nonconjugated diene; or
- (iv) 0 - 25% by weight of an acrylic-modified elastomer-based polymer wherein the elastomeric portion is polymerized from a monomer mixture containing at least 50% by weight of at least one C₁ to C₁₅ alkyl acrylate, 0 - 5% by weight of at least one graftlinking monomer, 0 - 5% by weight of a crosslinking monomer, and the balance to 100% by weight of at least other polymerizable ethylenically unsaturated monomer;
- provided that:
- (1) the total of (a) - (d) is 100%;
 - (2) the total polyester content of (a) and (d) (i) does not exceed 70%; and
 - (3) if (c) is 0%, then (d) cannot be (i), (iii) and (iv), and (ii) can be 10 - 45% by weight.

2. The composition of Claim 1 wherein the polybutylene terephthalate (a) has a number average molecular weight of at least 7500.
3. The composition of Claim 1 wherein the polymeric grafting agent (b) is a copolymer of at least 55% by weight ethylene, 1 - 10% by weight of an unsaturated epoxide of 4 - 11 carbon atoms, and 0 - 35% by weight of at least one of an alkyl acrylate or alkyl methacrylate wherein the alkyl group in each is from 1 - 8 carbon atoms.
4. The composition of Claim 2 wherein the polymeric grafting agent (b) is a copolymer of at least 55% by weight ethylene, 1 - 10% by weight of an unsaturated epoxide of 4 - 11 carbon atoms, and 0 - 35% by weight of at least one of an alkyl acrylate or alkyl methacrylate wherein the alkyl group in each is from 1 - 8 carbon atoms.
5. The composition of Claims 1, 2, 3 or 4 wherein the polymeric grafting agent (b) is selected from the group consisting of a copolymer of ethylene/n-butyl acrylate/glycidyl methacrylate, and a copolymer of ethylene/glycidyl methacrylate.

6. The composition of Claims 1, 2, 3 or 4 wherein ethylene copolymer (c) comprises at least 60% by weight of ethylene, 5 - 15% by weight of acrylic acid or methacrylic acid, and 0 - 25% by weight of a moiety selected from at least one of methyl acrylate, iso-butyl acrylate and n-butyl acrylate, and further wherein the acid groups are neutralized from 30 - 70% by at least one metal ion selected from lithium, potassium, sodium, zinc, aluminium, magnesium and calcium.
7. The composition of Claim 5 wherein ethylene copolymer (c) comprises at least 60% by weight of ethylene, 5 - 15% by weight of acrylic acid or methacrylic acid, and 0 - 25% by weight of a moiety selected from at least one of methyl acrylate, iso-butyl acrylate and n-butyl acrylate, and further wherein the acid groups are neutralized from 30 - 70% by at least one metal ion selected from lithium, potassium, sodium, zinc, aluminium, magnesium and calcium.
8. The composition of Claims 1, 2, 3 or 4 comprising:
- (a) 40 - 65% by weight of poly (1,4-butylene) terephthalate having a number average molecular weight of at least 7500;
 - (b) 2 - 30% by weight of a polymeric grafting agent which is a copolymer of at least 55% by weight ethylene, 1 - 10% by weight of glycidyl methacrylate, and 0 - 35% by weight of n-butyl acrylate;
 - (c) 0 - 20% by weight of an ethylene copolymer comprising at least 60% by weight of ethylene, 5 - 15% by weight of acrylic acid or methacrylic acid, and 0 - 25% by weight of a moiety selected from at least one of methyl acrylate, iso-butyl acrylate and n-butyl acrylate, and further wherein the acid groups are neutralized from 30 - 70% by at least one metal ion selected from sodium, zinc, magnesium and calcium;
- and
- (d) (i) 10 - 25% by weight of a copolyether ester which comprises a copolyether ester having 75% butyleneterephthalate units and 25% polytetramethylene ether (1000 Mn) terephthalate;
- provided that:
- (1) the total of (a) - (d) is 100%; and

- (2) the total polyester content of (a) and (d) (i) does not exceed 70%.

9. The composition of Claims 1, 2, 3 or 4 comprising:

- 5 (a) 50 - 60% by weight of poly (1,4-butylene) terephthalate having a number average molecular weight of at least 7500;
- (b) 5 - 15% by weight of a polymeric grafting agent which is a copolymer of at least 55% by weight ethylene, 1 - 10% by weight of glycidyl methacrylate, and 0 - 35% by weight of n-butyl acrylate;
- 10 (c) 0 - 10% by weight of an ethylene copolymer comprising at least 60% by weight of ethylene, 5 - 15% by weight of acrylic acid or methacrylic acid, and 0 - 25% by weight of a moiety selected from at least one of methyl acrylate, iso-butyl acrylate and n-butyl acrylate, and further wherein the acid groups are neutralized from 30 - 70% by at least one metal ion selected from sodium, zinc, magnesium and calcium;
- 15 (d) (ii) 20 - 45% by weight of a styrene/diene block copolymer, with 3 or more sequences, of the S-(D-S)_n structure where n is a whole number, S is a polystyrene block, D is a hydrogenated isoprenic block or hydrogenated butadienic block, with a content in styrene less than 50% by weight, optionally grafted with maleic anhydride.
- 20 provided that the total of (a) - (d) is 100%.

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10. The composition of Claims 1, 2, 3 or 4 comprising:

- (a) 50 - 65% by weight of poly (1,4-butylene) terephthalate having a number average molecular weight of at least 750
- (b) 5 - 15% by weight of a polymeric grafting agent which is a copolymer of at least 55% by weight ethylene, 1 - 10% by weight of glycidyl methacrylate, and 0 - 35% by weight of n-butyl acrylate;
- 30 (c) 5 - 10% by weight of an ethylene copolymer comprising at least 60% by weight of ethylene, 5 - 15% by weight of acrylic acid or methacrylic acid, and 0 - 25% by weight of a moiety selected from at least one of methyl acrylate, iso-butyl acrylate and n-
- 35

- 23 -

- butyl acrylate, and further wherein the acid groups are neutralized from 30 - 70% by at least one metal ion selected from lithium, sodium, zinc, aluminium, magnesium and calcium;
- (d) (iii) 10 - 25% by weight of an adduct of maleic anhydride and a copolymer of ethylene, propylene and at least one nonconjugated diene having a maleic anhydride content of 0.5 to 9% by weight and an inherent viscosity of at least 1, as measured on 0.1 gram of adduct dissolved in 100 milliliters of perchloroethylene at 30° C;
- provided that the total of (a) - (d) is 100%.

11. The composition of Claims 1, 2, 3 or 4 comprising:

- (a) 50 - 65% by weight of poly (1,4-butylene) terephthalate having a number average molecular weight of at least 7500;
- (b) 5 - 20% by weight of a polymeric grafting agent which is a copolymer of at least 55% by weight ethylene, 1 - 10% by weight of glycidyl methacrylate, and 0 - 35% by weight of n-butyl acrylate;
- (c) 5 - 15% by weight of an ethylene copolymer comprising at least 60% by weight of ethylene, 5 - 15% by weight of acrylic acid or methacrylic acid, and 0 - 25% by weight of a moiety selected from at least one of methyl acrylate, iso-butyl acrylate and n-butyl acrylate, and further wherein the acid groups are neutralized from 30 - 70% by at least one metal ion selected from sodium, zinc, magnesium and calcium; and
- (d) (iv) 15 - 25% by weight of an acrylic core//shell polymer having:
- (1) 70 - 80 parts by weight of a first acrylic elastomeric stage comprising a polymer polymerized from a monomer mixture comprising 79 - 99.5 parts n-butyl acrylate, 0 - 10 parts of at least one polymerizable monoethylenically or conjugated diethylenically unsaturated monomer, 0.1 - 5 parts 1,4-butylene glycol diacrylate and 0.1 - 5 parts diallyl maleate; and
- (2) 20 - 30 parts by weight hard shell final stage polymer polymerized in the presence of said first elastomeric

stage from a monomer mixture comprising about 80 - 100 parts by weight methyl methacrylate, 0 - 20 parts of another monoethylenically unsaturated monomer and 0 - 5 parts monoethylenically unsaturated carboxylic acid.

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12. The composition of claim 2 comprising:

(a) 40 -65% by weight of poly (1,4-butylene) terephthalate having a number average molecular weight of at least 7500;

10 (b) 2 - 30% by weight of a polymeric grafting agent which is a copolymer of at least 55% by weight ethylene, 1 - 10% by weight of glycidyl methacrylate, and 0 - 35% by weight of n-butyl acrylate;

(c) 0 -20% by weight of an ethylene copolymer comprising at least 60% by weight of ethylene, 5 - 15% by weight of acrylic acid or methacrylic acid, and 0 -25% by weight of a moiety selected from at least one of methyl acrylate, iso-butyl acrylate and n-butyl acrylate, and further wherein the aced groups are neutralized from 30 - 70% by at least one metal ion selected from sodium, zinc, magnesium and calcium; and

15 (d) (i) 5 -15% by weight of a copolyether ester which comprises a copolyester ester having 75% butyleneterephthalate units and 25% polytetramethylene ether (1000 Mn) terephthalate; and

(iv) 5 - 15% by weight of an acrylic core/shell polymer having:

(1) 70 -80 parts by weight of a first acrylic elastomeric stage comprising a polymer polymerized from a monomer mixture comprising 79 - 99.5 parts n-butyl acrylate, 0 - 10 parts of at least one polymerizable monoethylenically or conjugated diethylenically unsaturated monomer, 0.1 - 5 parts 1,4-butylene glycol diacrylate and 0.1 - 5 parts diallyl maleate; and

25 (2) 20 - 30 parts by weight hard shell final stage polymer polymrized in the presence of said first elastomeric stage from a monomer mixture comprising about 80 - 100 parts by weight methyl methacrylate, 0 - 20 parts of another monoethylenically unsaturated monomer and 0 - 5 parts monoethylenically unsaturated carboxylic acid.

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provided that:

- 25 -

- (1) the total of (a) - (d) is 100%; and
- (2) the total polyester content of (a) and (d) (i) does not exceed 70%.

5 13. The composition of Claims 1, 2, 3 or 4 comprising:

(a) 40 - 65% by weight of poly (1,4-butylene) terephthalate having a number average molecular weight of at least 7500;

(b) 2 - 30% by weight of a polymeric grafting agent which is a copolymer of at least 55% by weight ethylene, 1 - 10% by weight of glycidyl
10 methacrylate, and 0 - 35% by weight of n-butyl acrylate;

(c) 0 - 20% by weight of an ethylene copolymer comprising at least 60% by weight of ethylene, 5 - 15% by weight of acrylic acid or methacrylic acid, and 0 - 25% by weight of a moiety selected from at least one of methyl acrylate, iso-butyl acrylate and n-butyl acrylate, and further wherein the acid
15 groups are neutralized from 30 - 70% by at least one metal ion selected from sodium, zinc, magnesium and calcium; and

(d) (i) 5 - 15% by weight of an ethylene copolymer comprising at least 60% by weight of ethylene, 5 - 15% by weight of acrylic acid or methacrylic acid, and 0 - 25% by weight of a moiety selected from at least one of methyl
20 acrylate, iso-butyl acrylate and n-butyl acrylate, and further wherein the acid groups are neutralized from 30 - 70% by at least one metal ion selected from sodium, zinc, magnesium and calcium;

(iii) 5 - 15% by weight of an adduct of maleic anhydride and a copolymer of ethylene, propylene and at least one nonconjugated diene
25 having a maleic anhydride content of 0.5 to 9% by weight and an inherent viscosity of at least 1, as measured on 0.1 gram of adduct dissolved in 100 milliliters of perchloroethylene at 30° C;
provided that:

- (1) the total of (a) - (d) is 100%; and
- (2) the total polyester content of (a) and (d) (i) does not
30 exceed 70%.

14. The composition of Claims 1 - 11 wherein the total polyester content does not exceed 65% by weight.

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15. An insulated wire comprising an electrically conductive wire having a coating thereon the composition of and of Claims 1 - 11.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/08956

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.C1.5 C 08 L 67/02 C 08 G 81/02 H 01 B 3/42 //
(C 08 L 67/02 C 08 L 23:08 C 08 L 67:02) (C 08 L 67/02 C 08 L 23:
08 C 08 L 75:06) (C 08 L 67/02, 23:08, 53:02) (C 08 L 67/02, 23:08)

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System

Classification Symbols

Int.C1.5

C 08 L

C 08 G

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	Chemical Abstracts, vol. 107, no. 12, (Columbus, Ohio, US), see abstract no. 97740e, & JP,A,62034951 (TORAY IND.) 14 February 1987, see abstract ---	1-5,9
P,X	Chemical Abstracts, vol. 116, no. 12, (Columbus, Ohio, US), see abstract no. 107636c, & JP,A,3250044 (NIHON GE PLASTICS, LTD) 7 November 1991, see abstract ---	1-5,9
P,X	WO,A,9119767 (DU PONT DE NEMOURS) 26 December 1991, see claims 1,2; page 10, line 5 - page 16, line 19 --- -/-	1-5,8

¹⁰ Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

05-02-1993

Date of Mailing of this International Search Report

10.03.93

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

D.H. KRISCHE

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	WO,A,8803543 (DU PONT DE NEMOURS) 19 May 1988, see claims 1,2,5-12; page 1, line 10 - page 3, line 22; pages 31-34; page 82, example 88 (cited in the application) ---	1-7,15
A	WO,A,9113119 (EXXON CHEMICAL) 5 September 1991, see claims 1-5,10,12; page 12, line 20 - page 15, line 36; page 18; examples 1,2 ---	1-5,10
A	EP,A,0420017 (BASF) 3 April 1991, see claims 2,3,5-8; example 11; page 8, line 21 - page 9, line 28 ---	1-5
A	Chemical Abstracts, vol. 105, no. 20, (Columbus, Ohio, US), see abstract no. 174065b, & JP,A,61148261 (TORAY IND.) 5 July 1986, see abstract -----	1-5,8

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9208956

SA 66060

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 17/02/93
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A- 9119767	26-12-91	US-A- 5091459 US-A- 5128404	25-02-92 07-07-92
WO-A- 8803543	19-05-88	EP-A- 0290588 JP-T- 1501713 US-A- 5091478	17-11-88 15-06-89 25-02-92
WO-A- 9113119	05-09-91	None	
EP-A- 0420017	03-04-91	DE-A- 3932360 CA-A- 2026383 JP-A- 3166257	11-04-91 29-03-91 18-07-91

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82